

"Artificial" superconductors. Superconducting phases in the Mg_xWO_3 nanocomposite ($x = 0.037; 0.125 - T_{cx} = 140; 280 \text{ K}$).

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Superconductivity of some compounds may be explained as resulting from Bose-Einstein condensation (BEC) of atomic electron pairs of divalent atoms or electron pairs of diatomic molecules made up of univalent atoms. "Artificial" superconductors of such types can be tailored using non-stoichiometric compounds. Synthesis of "natural" stoichiometric superconductors is a much more complicated problem. In these cases, we have two methods of obtaining dilute metals in a state intermediate between the metal and the insulator.

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Preparation of materials with preset properties appears simplest and easiest to understand in the case of nonstoichiometric compounds - nanocomposites [1]. This case may be illustrated by arrays of nanostructures embedded in voids of zeolites, asbestos, porous glasses, and opals (cluster superlattices) [2, 3, 4]. Another group of similar systems combines matrices whose voids can accommodate sublattices of separate atoms only. This group approaches stoichiometric compounds. Actually, it is at the edge of valence interactions between the matrix-filler sublattices. Take, for instance, Na_xWO_3 , which for $x > 0.33$ becomes a well known tungsten bronze.

Our choice of the Mg_xWO_3 nanocomposite ($x < 0.4$) may serve as an illustration of a simple physico-chemical tailoring of superconductors. The filler in the WO_3 matrix was Mg ($2r_{\text{Mg}} \sim 3.3 \text{ \AA}$; the electron pair is formed by two s electrons. $\Delta_c \sim (7.6/20) \text{ eV}$, $T_{cmax} \sim 600 \text{ K}$ for $x \sim 0.4$) [1].

The Mg metal in the Mg_xWO_3 system is diluted by insulator in accordance with the value of x [5]. Figure 1a shows schematically the WO_3 cell with the parameters $a \sim b \sim c \sim 3.78 \text{ \AA}$. The void diameter is $\sim 3.8 \text{ \AA}$ (Fig. 1c,d). The Mg atom diameter $d_{\text{Mg}} \sim 3.3 \text{ \AA}$. The diameter of the "windows" is $\sim 2.7 \text{ \AA}$ (Fig. 1b). Therefore, penetration of Mg atoms through the windows meets with difficulties, which makes Mg_xWO_3 stable. The Mg- WO_3 contact is close to valence interactions, because the metal-insulator phase gap is usually $\sim (0.5 - 0.7) \text{ \AA}$ [6].

Figure 2 plots the temperature dependence of the resistance, $R(T)$, of a sample of pressed powder ($\text{MgO}, \text{WO}_2, \text{WO}_3$) containing several "perovskite type" $\text{Mg}_{(0.037-0.125)}\text{WO}_3$ phases. (The sample was prepared by A. V. Golubkov.) One immediately sees several transitions in the $100 - 300 \text{ K}$ range. The Meissner effect was not observed because of the presence of nonsuper-

conducting phases.

Mg_xWO_3 is a nanocomposite, and it differs from MgB_2 , in which Mg is diluted "chemically" but which still remains a metal with BCS superconductivity.

The cubic void array of WO_3 can accommodate several regular and equilibrium sublattices of Mg atoms with a cell volume V_1 and the number x of Mg atoms per WO_3 cell ($\sim a^3$) Fig. 2. In the case of BEC, to each value of x corresponds $T_{cx} \sim x^{2/3} \sim n_2^{2/3}$. For $x = 0.125$ ($V_1 = 2^3 a^3$), the electron pair concentration is $n_2 = 23 \cdot 10^{20} \text{ cm}^{-3}$, and $T_{cx} \sim 290 \text{ K}$ ($m^* \sim 10m_e$ [1]). The Table lists also experimental values of T_{cexp} , which are close to T_{cx} (Figs. 2 and 3).

V_1	a^3	$2(a)^3$	$(2a)^3$	$2^2 3(a)^3$	$2(2a)^3$	$(3a)^3$	$2(3a)^3$
x	1	0.5	0.125	0.083	0.063	0.037	0.019
$T_{cx} \text{ K}$?	?	290	225	185	130	76
$T_{cexp} \text{ K}$	—	—	280	240	175	140	< 78?

A condensate of Mg atoms which practically do not interact with the matrix may serve as a model for a system with Bose-Einstein electron pair condensation [5]. Matrices similar to WO_3 and corresponding standard technologies for perovskites and spinels may be used to accommodate other electron-pair atoms to tailor new "artificial" superconductors (for instance, a spinel MgAl_2O_4). The first attempt at synthesizing an "artificial" superconductor was undertaken by Ogg in 1946 (NaNH_3) [7]. Tailoring of stoichiometric ("natural") superconductors is an issue of formidable complexity. It will possibly require invoking computer simulation [8]. Development of "artificial" and "natural" superconductors may be considered as essentially two methods of obtaining dilute metals in a state intermediate between the metal and insulator [1, 9, 10].

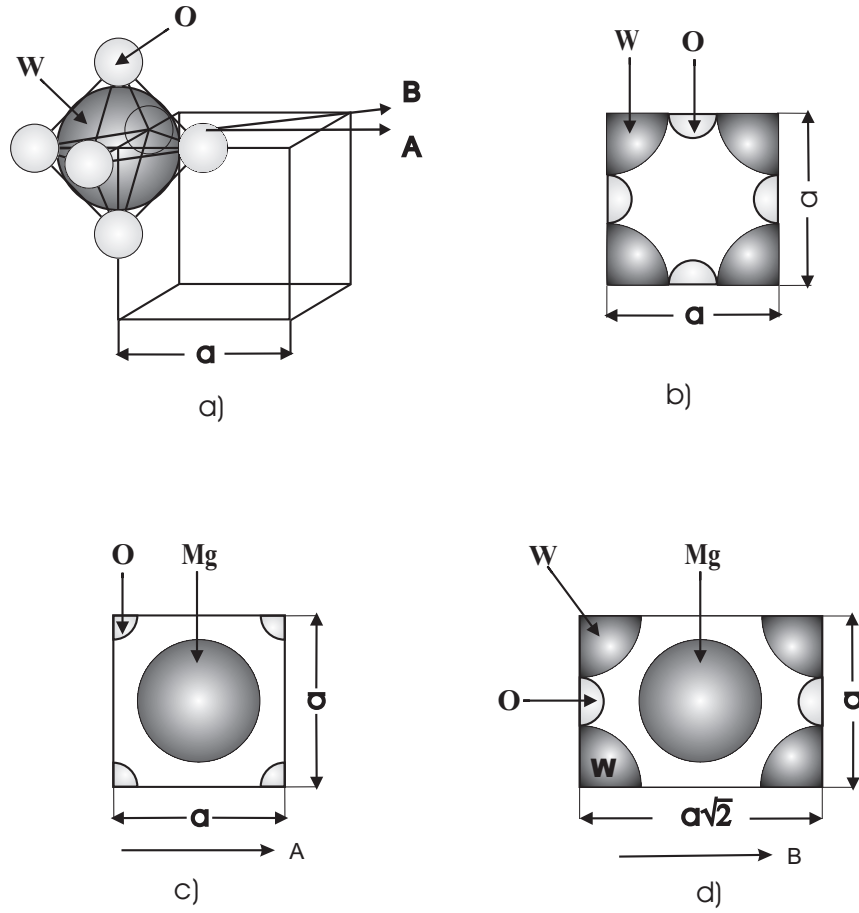


FIG. 1: WO_3 cell (a);
Side face of WO_3 cell (b);
Section of Mg-WO_3 cell along the A direction (c);
Section of Mg-WO_3 cell along the B direction (d);

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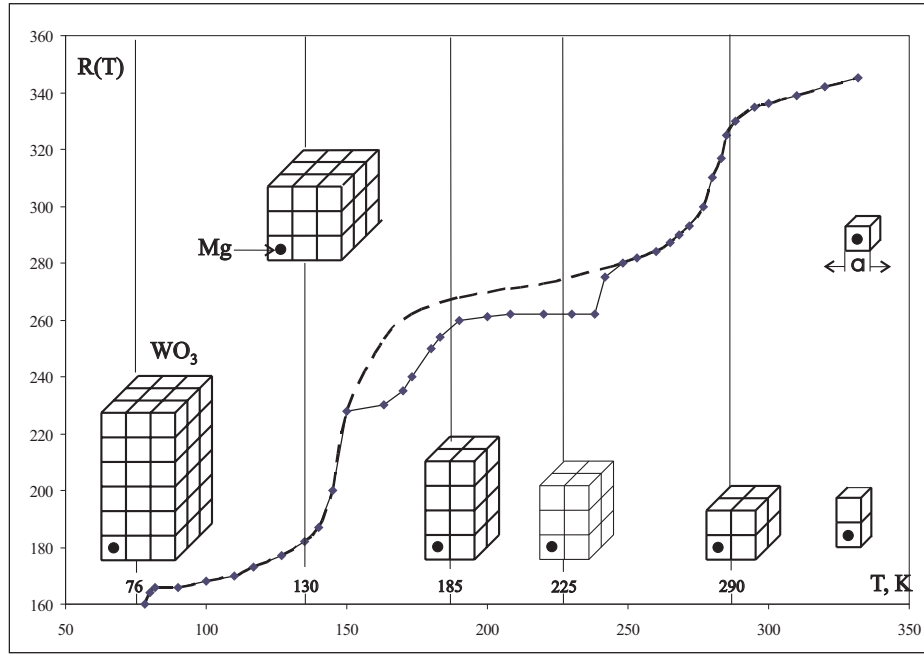


FIG. 2: Temperature dependence of the resistance of a Mg_xWO_3 sample.

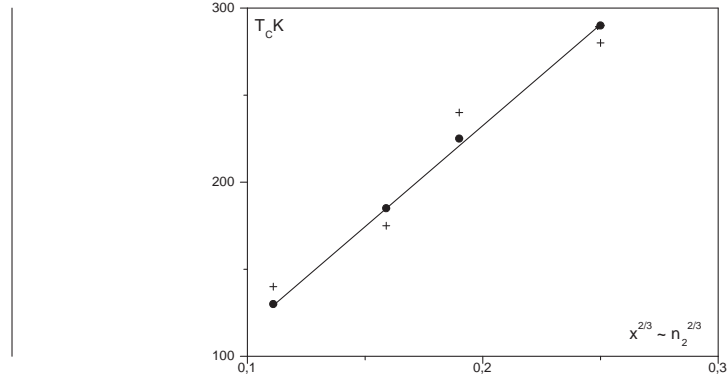


FIG. 3: Dependence of T_c on $x^{2/3} \sim n_2^{2/3}$. The same dependence is observed in $\text{SrNb}_x\text{Ti}_{1-x}\text{O}_3$ [5].
 T_{cx} - point; T_{cexp} - cross.